Forest Research
Technical Report
Vancouver Forest Region
2100 Labieux Road, Nanaimo, BC, Canada, V9T 6E9, 250-751-7001

TR-013 Hydrology March 2001

Roberts Creek Study Forest: Pre-harvest chemical characteristics of three S6 creeks, Flume Creek Experimental Watershed

by

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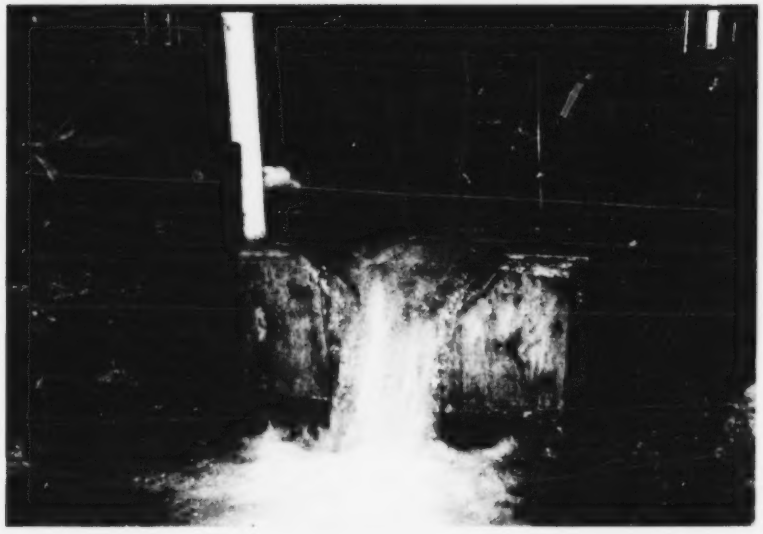

Research Disciplines: Ecology ~ Geology ~ Geomorphology ~ Hydrology ~ Pedology ~ Silviculture ~ Wildlife

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Cover Photo: Weir built on Flume Creek to assist in water sampling and streamflow measurement; the creek is at medium flow in this photo.

ABSTRACT

Pre-treatment water chemistry was analysed for three small S6 creeks in the Flume Creek watershed, part of the Roberts Creek Study Forest. The objective was to create a baseline for the future assessment of the water chemistry impacts of partial harvesting systems.

The chemicals studied are derived primarily from chemical weathering, biological activity and atmospheric sources. Analysis indicated that water chemistry was controlled by time during the season, suggesting a buildup of stored chemicals over the dry summer months, followed by a period during which the chemicals are leached from the watershed faster than the rate at which they can be replenished. Within storm events, there is a dilution effect that also influences concentrations. These effects interact, resulting in highly complex relationships between chemical concentrations, streamflow and seasonal factors.

1.0 INTRODUCTION

Water quality has long been a concern to residents of the Sunshine Coast. In particular, the Roberts Creek area supports a large rural community, and many residents depend on small creeks for their water supply. There is a perception that forest harvesting and related activities (specifically clear-cut harvesting) might alter water quality in those creeks. There is also a perception that the use of partial harvesting systems might serve to lessen those effects. In an effort to address those concerns, the Flume Creek Paired Watershed Experiment was implemented. The purpose of this paper is to report on base line water chemistry conditions observed in the Flume Creek study watersheds, to provide the basis for assessing any changes in water chemistry that occur as a result of harvesting.

A large number of watershed studies on the effects of clear-cut harvesting have been reported in the literature. The classic study by Likens et al. (1970, 1977, 1978) at Hubbard Brook in New Hampshire documented large changes in water chemistry. A subbasin of Hubbard Brook was entirely clear-cut and vegetation regrowth was suppressed with herbicides for a period of two years following harvesting. This treatment resulted in large increases in base cations, hydrogen ion (i.e., reduced pH), nitrate and chloride, as well as an eight-fold increase in Al^{3+}. There was a corresponding decrease in sulphate. Subsequently, Likens et al. (1978) presented a mechanism to explain the increases. The temperature and water content of the forest floor were increased following clear-cutting due to reduced shade and evapotranspiration, resulting in an increased rate of organic matter decomposition (bacterial conversion of organic nitrogen to NH_4^+) and nitrification (conversion of the mineralized NH_4^+ to NO_3^- and NO_2^- by different bacteria). Nitrification produces hydrogen ion, lowering stream pH and mobilizing base cations. The occupation of cation exchange sites by H^+ causes sulphate to adsorb to the soil, explaining the reduction in sulphate in streamflow (Nodvin et al., 1988).

In comparison, Martin et al. (1984) studied 15 streams in New England (some unlogged, some with recent logging varying from 16 to 100 % of their area) with different results. The study was based on comparative sampling of creeks logged within two years of the study, with nearby uncut watersheds having similar characteristics. The authors did not find the kind of impacts on stream chemistry that were found at Hubbard Brook. Some logged streams experienced slight changes in pH, Ca and Mg, but not others. Nitrogen in streams rose following clear-cutting only in the vicinity of the White Mountains where Hubbard Brook is located. The failure to detect significant chemical changes was attributed to the following factors: most watersheds were harvested in stages; most were not 100% clear-cut, so that nutrient uptake in uncut areas or streamside buffer strips may have moderated the impacts in the harvested areas; and soil types in the study creeks may have buffered the impacts. Martin et al. (1985) stress the role of patch or strip cutting or the use of buffers wider than 9 m on each side of the stream in reducing the impacts on stream chemistry.

Nitrate export is one of the most important indicators of watershed disturbance due to logging. Binkley and Brown (1993) reviewed several North American studies that examined the impacts of forest management practices on nitrate concentra-

Summary of chemical notations used in this report:

Chemical	Notation	Chemical	Notation
calcium	Ca^{2+}	manganese	Mn^{2+}
sodium	Na^{+}	ammonium	NH_4^{+}
magnesium	Mg^{2+}	chloride	Cl^{-}
potassium	K^{+}	nitrate	NO_3^{-}
aluminum	Al^{3+}	nitrite	NO_2^{-}
boron	B^{3+}	phosphate	PO_4^{2-}
iron	Fe^{3+}	sulphate	SO_4^{2-}
zinc	Zn^{2+}	silica	SiO_4
copper	Cu^{2+}	bicarbonate	HCO_3^{-}

KEY WORDS

water chemistry, water quality, Roberts Creek Study Forest, Sunshine Coast.

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ACKNOWLEDGMENTS

This research was funded by the Ministry of Forests Operations Division base funding, under the Silvicultural Systems research program. Several people contributed field work. John Tyler and Karen Paulig built the weirs. John Tyler and Julie Orban assisted with sampling and instrument maintenance. Chemical analysis was done at the Glyn Road lab operated by theMinistry of Forests Research Branch under the supervision of Clive Dawson. Ryanne Metcalf assisted with pH and bicarbonate analysis and data compilation.

tions, as well as temperature, dissolved oxygen, and suspended sediment. About 70% of the studies reported that mean annual nitrate concentrations were below 0.5 mg/l for both harvested and control watersheds. Exceptions were in the red alder (Alnus rubra) and Douglas-fir (Pseudotsuga menzesii) forests in Oregon, where equally high levels of nitrate existed in the control and treatment watersheds, and in the hardwood forests of Hubbard Brook. Vitousek et al. (1982) determined that the observed changes in nitrate at Hubbard Brook were due to proliferation of both mineralizing and nitrifying bacteria. If mineralizing bacteria were not present or in limited supply, the changes would not occur. If mineralizing bacteria were present, but not nitrifying bacteria, there would be a delay in increased nitrate that could be sufficient to allow forest regeneration to prevent any increase in nitrate concentration in streams.

Gibbs (1970) suggested that the world's water chemistry is controlled by precipitation, mineral weathering, and evaporation-crystallization, and that other mechanisms are minor in comparison. Vitousek (1977) suggested that in humid climates, evaporation-crystallization is replaced by evapotranspiration, and that those control processes affect specific chemical species differently. In the northeastern United States, sulphate and chloride are controlled by precipitation and evapotranspiration, while sodium, silica, magnesium, and calcium are controlled by mineral weathering, and nitrate and potassium are controlled by plant uptake. Johnson and Reynolds (1977) showed that bedrock type has a major influence on stream chemistry in its weatherability. Plutonic rocks (e.g. granite) are acidic, with anions dominated by sulphate and chloride, and are least weatherable, producing low concentrations of base cations and silica. Highly weatherable sedimentary rocks, such as shale, produce the highest concentrations of base cations with the dominant anion being bicarbonate.

Cronan *et al.* (1978) proposed that ecosystems could be divided into categories based on the dominance of SO_4^{2-}, HCO_3^-, or organic anions in streamflow. Studies conducted at Hubbard Brook (e.g. Likens *et al.*, 1970) showed that sulphate is the dominant anion at that location. Cronan *et al.* suggested that this could be attributed to heavy acidification on already acidic terrain. Thorne *et al.* (1988) proposed that bicarbonate-dominated ecosystems be subdivided into those where HCO_3^- is produced by the dissolution of CO_2 from soil respiration, and those where HCO_3^- is generated from weathering of carbonate rocks, the latter being better buffered than the former. Hazlett *et al.* (1992), in a study at Turkey Lakes watershed in northern Ontario, noted high concentrations of hydrogen ion, calcium, sulphate, and nitrate in forest floor percolates during the early phases of snowmelt, with a subsequent decrease in concentrations as the melt season progressed. High chemical production at the start of snowmelt was attributed to over winter mineralization of sulphur and nitrogen in the forest floor, with the subsequent decline in concentrations attributed to progressive leaching of those chemicals. These trends were also observed in the mineral soil, with the exception of sulphate. The initial pulse of H^+ from snowmelt was thought to have mobilized the Ca^{2+} ions from cation exchange sites in the mineral soil.

Different processes act on water to modify its chemistry at different stages. Processes that occur in the forest floor and organic soil horizons include mineralization due to biological action (e.g., Hazlett et al., 1992, Hendershot et al., 1992, Feller, 1977). Groundwater chemistry tends to be governed by mineral weathering with concentrations influenced by weatherability as discussed above, and residence time (Jacks & Paces, 1987, Denning et al., 1992, Hendershot et al., 1992, Hudson & Golding, 1997a). Relationships between streamflow and concentrations of base cations and silica are well defined where mineral weathering is the main control on those chemicals (Hudson & Golding, 1997b), but less well defined when other factors influence those chemicals (Feller and Kimmins, 1979).

As noted above, the effects of clear-cut logging on water chemistry have been studied extensively, but the effects of partial harvesting are still largely unknown. In order to gain some understanding of the relative effects of partial harvesting on water chemistry, the Flume Creek Paired Watershed Experiment was implemented in the early 1990s as part of the Roberts Creek Study Forest.

The Roberts Creek Study Forest (RCSF) is located on the southwestern flank of Mount Elphinstone on the Sunshine Coast approximately 40 km northwest of Vancouver, BC (Figure 1). The RCSF is a collection of adaptive management case studies demonstrating a range of cutting patterns in blocks designed to assist the development of future silviculture prescriptions in the lower elevation, naturally regenerated Douglas-fir dominated ecosystem of the southern coast of the mainland. The Flume Creek Paired Watershed Experiment is one component of the RCSF, and was implemented to investigate the effects of two partial harvesting systems on streamflow and water quality in small S5 and S6 creeks.

2.0 STUDY AREA

The Mount Elphinstone slope is relatively uniform and dissected by first-order creeks that drain narrow elongated catchments. The interfluves between these first-order creeks are further dissected by zero-order creeks. A zero-order creek is difficult to identify through the forest cover on air photos, and therefore generally does not appear on maps. It is ephemeral, and does not occupy a clearly defined gully, but nonetheless is capable of carrying very substantial flows. In contrast, first-order creeks are perennial and are clearly visible on air photos because they normally occupy gullies.

The Flume Creek Experimental Watershed consists of three small catchments, designated as F4, F5 and F6 (Figure 1), that are typical of the type of drainage pattern described above. All three creeks are classed as S6 under the Forest Practices Code of BC Act and Regulations. F4 and F6 creeks are zero-order, whereas F5 is a first-order creek at the outlet, with several zero-order tributaries. The zero-order creeks typically go dry in June or July. The first-order channel of F5 usually does not go completely dry, but flow reduces to an unmeasurable trickle. The creeks do not start to flow again until soil moisture is recharged in the fall; this usually requires several rain storms. For example, in 1996 the creeks did not start to rise until mid October.

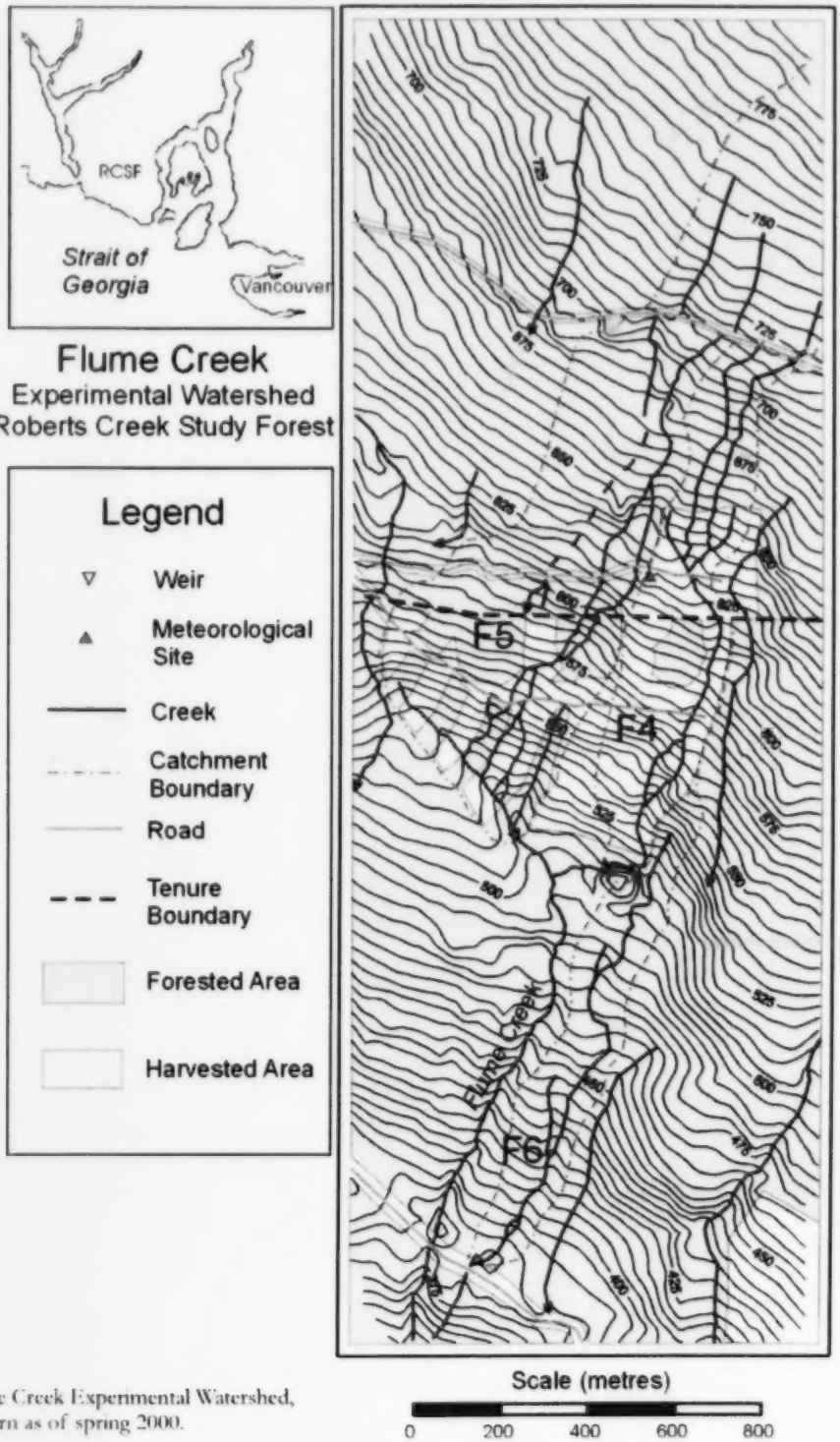

Figure 1. Map of study area: Flume Creek Experimental Watershed, showing the forest harvesting pattern as of spring 2000.

F6 drains an area of 16 hectares and ranges in elevation from 395 to 560 metres above sea level, with a mean channel gradient of 13%. F4 and F5 range from 505 to about 850 metres above sea level, with drainage areas of 39 and 61 hectares respectively. F4 has a mean channel gradient of 17%. The first-order channel of F5 has a gradient of 6.5%, while the zero-order tributaries have an average gradient of 18%. All zero-order channel gradients reflect the local land slope.

S6 creeks are generally not a major concern for forest managers (they do not support fish, and water licenses are usually on larger streams). Nonetheless, S6 creeks were selected for the study in order to carry out a standard paired watershed experiment within the operational forest management strategy of the Sunshine Coast Forest District. Because the target maximum block size is 10 hectares, it was necessary to study small catchments to achieve a canopy removal that is likely to produce a measurable effect. Nonetheless, it is at the level of the S6 creek where the primary effects of forest harvesting occur, since S6 creeks are tributary to larger creeks where the water licenses are located. Any changes that are observed at this level will be reduced by the effect of dilution in larger creeks, and as the rate of cut in a watershed increases, the effect at downstream points will approach the effect observed at the S6 level.

3.0 METHODS

3.1 MEASUREMENT OF STREAMFLOW

Each creek is equipped with a weir for flow measurement (see cover photo). The weirs are constructed of concrete with a plywood wall at the downstream end to which a sharp crested metal weir plate is attached. The weir plate has a central 90° V-notch section to allow for precise measurement of low flows, but also has a rectangular overflow section to accommodate high flows. The V-notch section has a head of about 0.25 metres, and the rectangular section has a head of about 0.5 metres above the V-notch section.

At F4 and F5, the weirs were constructed in straight channel reaches, in late summer when the channels were dry. The channels were deepened, and plywood forms were built into which concrete was poured. The plywood was removed after the concrete had dried. At F6, the creek flows into the ditch as it leaves the forest above the road, and from there flows through a culvert. Therefore, instead of setting the weir into the channel, two retaining walls were constructed in the ditch to create a pond. The weir plate is set into one of the walls. Otherwise, the weir was constructed as described above. F5 and F6 were built in September 1994 and F4 in the summer of 1995.

The weirs have been calibrated (Cathcart, 1997) and provide very precise flow measurement based on calibration equations that relate flow to the head of water over the weir crest. Each one is equipped with a staff gauge located at the upstream end of the structure and corrected to the weir crest. At each site, stage is measured with a Unidata capacitive water depth probe and average values are recorded on a Unidata "Macro" 7000 data logger at a log interval of 15 minutes. The resolution of this instrumentation is ± 1%.

3.2 SAMPLING

Each weir was equipped with an ISCO 3700C automatic pump sampler. The samplers were activated by a signal from the data logger, based on changes in stage. That is, each time a predetermined change in stage occurred, either rising or falling, the data logger would send a pulse to the sampler, which would collect a sample and then wait for the next signal. The sampler can collect and store up to 24 samples in 500 ml sample bottles. The rise and fall of discharge was used to trigger the samplers in order to obtain samples for a range of flows, and to sample more frequently during storms.

Generally, the samples were retrieved from the sampler every one to two weeks, depending on storm activity. Samples were collected in duplicate by transferring the sample from the sampler bottles into clean 150 ml polypropylene bottles. One set of samples was frozen for analysis at the Ministry of Forests Research Branch analytical lab in Victoria. These samples were analyzed for concentrations of cations calcium, sodium, magnesium, potassium, aluminum, boron, iron, zinc, copper, manganese, ammonium, anions chloride, nitrate, phosphate, and sulphate, and the non-ionic silica, total soluble nitrogen, and total soluble sulphur. The second set was used to measure pH and bicarbonate concentration, which was done in-house.

3.3 CHEMICAL ANALYSIS

Bicarbonate was measured by potentiometric titration to a predetermined pH end point, using weak (0.001 N) hydrochloric acid. The end points were different for each creek, and were determined initially by doing a full titration. For the analysis of major anions and cations, the samples were kept frozen at -80 degrees C prior to analysis. The samples were thawed and allowed to equilibrate to room temperature. Sub-samples were poured off for ICP and ion chromatography analysis. The sub-samples were re-frozen at -80 and thawed as required during analysis.

Cations except ammonium were measured on the ARL 3560 ICP using off-peak background correction and subsequent subtraction of a Milli-Q (18 megohm) water blank to compensate for any plasma on-peak interference. The ICP was calibrated using NIST traceable ICP calibration standards.

Major cations and anions were analyzed by ion chromatography using a Waters 'Action Analyzer' HPLC system. The cations were separated on a Waters IC-Pak Cation M/D column and detected by conductivity. The anions were separated on a Waters IC-Pak Anion HR column and detected by conductivity, except for nitrate which was detected by a UV/visible detector for better detection limits. Calibration was done using NIST traceable ion chromatography standards.

Where the same ions were analyzed by both methods, the agreement was excellent. For Ca^{2+}, Mg^{2+} and Na^{+}, the results from the two techniques were averaged. Potassium results were much better from the ion chromatograph and therefore those values were reported. Al^{3+}, B^{3+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, P, Ssol, Si and Zn^{2+} are ICP values. Cl^{-}, NH_4^{+}, NO_3^{-}, PO_4^{3-}, and SO_4^{2-} are ion chromatography results. SiO_2 was a calculated value based on the Si ICP result.

3.4 DATA ANALYSIS.

Various analytical methods were used to arrive at the relationships that describe the chemical behaviour of the three study creeks. The main methods were correlation, stepwise regression, and best subsets regression (Minitab, Inc., 1995).

As an initial step in identifying potential independent variables to use as predictors of chemical concentrations, all the potential variables were intercorrelated. Ideally, a good predictive model is one in which the independent variables are poorly correlated with each other, but are well correlated with the dependent variable. The potential predictors are discussed in the next section. Interactions between the independent variables were also considered, as were transformations (in particular, the streamflow data were log transformed, and expressed on a per-hectare basis).

As a second step, stepwise regression analysis was used to select the best possible set of predictor variables. However, stepwise regression often results in a different model for each chemical and for each creek, depending on the complexity of the relationships. For example, base cation behaviour is expected to be the same for each creek and for each cation, thus it is reasonable to expect the models of base cation concentration to have a common form. Therefore, the next step in model identification was to use best subsets regression to derive common models for the chemicals that were expected to exhibit similar behaviour. The final step in the process was to perform the regression analysis for each chemical on each creek to derive an equation. The validity of the regression equation was checked by plotting the residuals against the predicted values. If the residuals were randomly distributed with respect to the fitted values, then the model was accepted.

Because the chemical analysis included trace elements, a decision was made to ignore any chemicals whose mean concentrations in streamflow were less than 0.05 mg/L.

4.0 RESULTS

4.1 GENERAL TRENDS IN CHEMICAL CONCENTRATIONS

The water in Flume Creek was of low ionic strength. The major anions were bicarbonate and sulphate, and the major cations were calcium, magnesium and sodium (Table 1). Observed patterns were the same in all three creeks, although concentrations did vary slightly from site to site.

The maximum concentrations of Ca, Cl, Mg, Na, NO_3 and Si were observed during the fall freshet (Figures 2, 3 and 4). As the streams first start to rise in response to fall rains, there is an initial concentrated flush of chemicals from the soil, followed by a dilution effect as the streamflow increases. The cations and silica are weathering products and the nitrate a product of biological activity, and presumably were produced and stored in the soil over the summer. After the initial event, the trend for both storm-averaged concentration and individual sample concentrations was a general decrease through the rainy season to a mini-

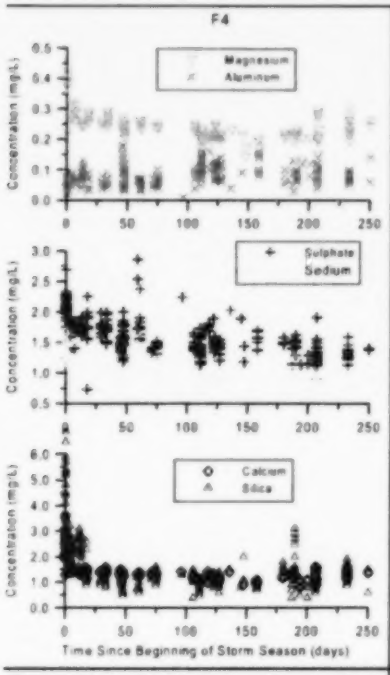

Figure 2. Chemical concentrations vs. time since beginning of season, F4 watershed.

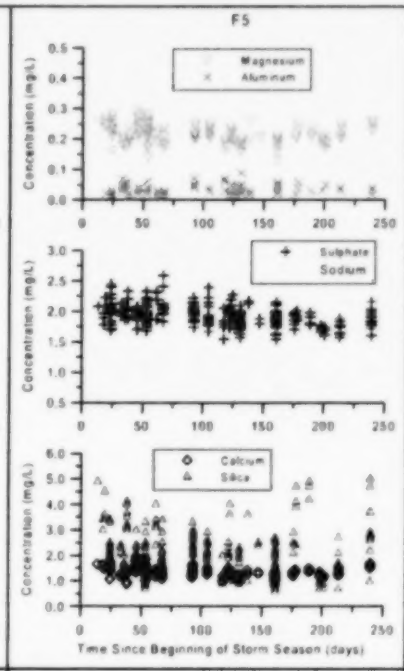

Figure 3. Chemical concentrations vs. time since beginning of season, F5 watershed.

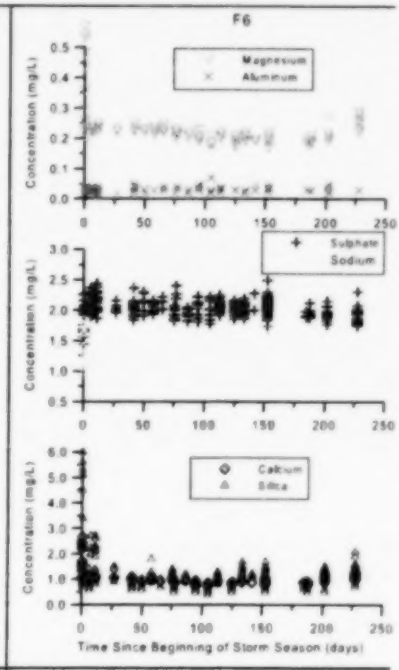

Figure 4. Chemical concentrations vs. time since beginning of season, F6 watershed.

mum during late winter storms. This is due to a gradual depletion of chemicals from the soil as the season progresses. Where samples were obtained for late spring and early summer storms, concentrations were seen to rise again (Figures 2, 3 and 4).

This rise in concentration occurs at a time when conditions are more favourable to both biological activity and chemical weathering, since both are related to temperature.

Within individual storms, there were relationships between chemical concentrations and streamflow superimposed on the seasonal effect noted above. Al^{3+} showed the most consistent variability during storms. At F4, Al^{3+} was positively correlated with streamflow, while at F5 and F6 there was no relationship between Al^{3+} concentration and streamflow, and at all three sites the seasonal trend was absent. Base cation concentrations showed complex behaviour, responding to the seasonal effect and to storms. Concentrations were generally negatively correlated with streamflow, but not always. For example, at F4, Ca^{2+} concentrations were positively related to streamflow during the first storm of the season. During subsequent storms, the slope of the relationship between concentration and the log of streamflow became negative, and increasingly so as the storm season progressed. After a long dry period, a positive slope would be re-established, and the pattern would repeat itself.

However, relationships between concentration and discharge were generally very poorly defined for most storms. Plots of concentrations against the natural logarithm of the flow during storms showed a hysteresis effect, with the concentration higher on the rising limb of the hydrograph than on the falling limb.

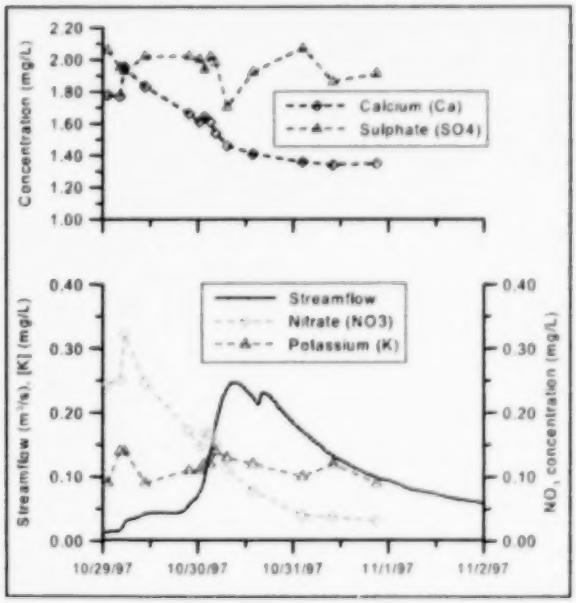

Figure 5. Streamflow and concentrations of nitrate, calcium, sulphate and potassium at F5 in response to October 29, 1997 storm. This is the fall freshet for 1997.

Table 1. Summary – pre-treatment average concentrations

Chemical	F4	F5	F6
HCO_3	2.83	3.23	1.91
SO_4	1.59	1.92	2.03
SiO_4	1.50	1.99	1.18
Ca	1.36	1.33	0.98
Na	0.98	1.00	1.07
Cl	0.97	1.11	1.14
Soluble S	0.53	0.61	0.66
Mg	0.25	0.23	0.22
PO_4	0.15	0.00	0.91
NO_3	0.10	0.07	0.09
K	0.08	0.09	0.09
Al	0.08	0.03	0.03
P	0.05	0.04	0.06
Fe	0.02	0.01	0.01
NH_4	0.02	0.04	0.02
Zn	0.02	0.03	0.02
B	0.01	0.02	0.00
Mn	0.01	0.02	0.00
Cu	0.00	0.01	0.01
Soluble N	0.00	0.00	0.00

These patterns were also observed for magnesium. Patterns of sodium behaviour were similar, with high concentrations occurring during the freshet (Figures 2, 3 and 4), but were generally less well correlated with streamflow than calcium and magnesium. Hysteresis was observed during storms at F5, but not at F4 or F6. Potassium concentration was not related to streamflow, and the only significant relationship that could be identified was a seasonal difference in average concentrations.

Bicarbonate behaviour was less complex than that of the base cations. There did not appear to be a hysteresis effect, and the high concentrations during the freshet were not observed. Relationships between concentration and streamflow were better defined than with most other chemicals; concentrations decreased with increasing streamflow. Sulphate was generally positively correlated with streamflow during storms. Nitrate behaviour was complex; typically, nitrate exhibited pulse behaviour during storms. That is, nitrate concentrations normally peaked on the rising limb of the hydrograph, and began to decline again before the occurrence of the peak flow. The concentration peaks of these pulses were highest in the early part of the season and declined throughout the season as with other chemicals. To a certain extent, potassium concentrations also experienced pulse behaviour, but maintained relatively constant concentrations overall.

This complexity of behaviour can be demonstrated by examining individual storms at different times in the season. For example, three storms on F5 were selected for this purpose: a "freshet" storm that occurred on October 29, 1997, a mid-season storm on January 23, 1998, and a large spring storm on March 18, 1997 (Figures 5, 6 and 7, respectively). In the freshet

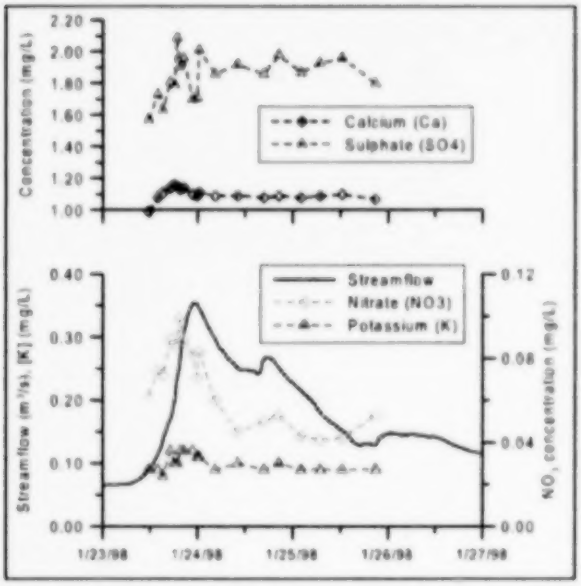

Figure 6. Streamflow and concentrations of nitrate, calcium, sulphate and potassium at F5 in response to January 23, 1998 storm. This is a mid-season storm. Note that the axis depicting nitrate concentration has changed.

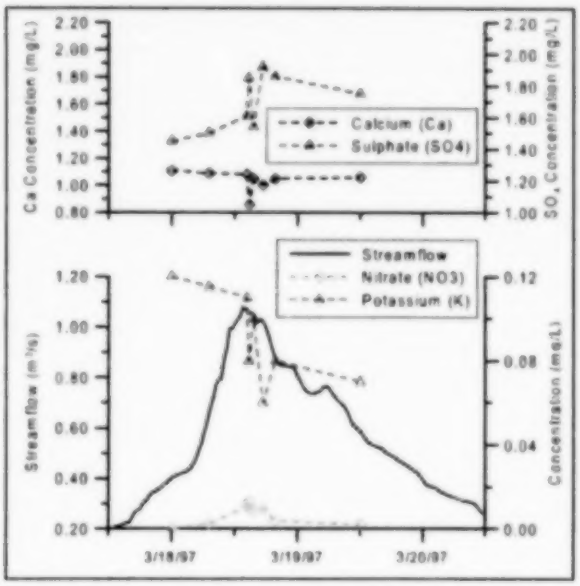

Figure 7. Streamflow and concentrations of nitrate, calcium, sulphate and potassium at F5 in response to March 18, 1997 storm. This is a late season storm. Note that the axis for streamflow has changed. This is one of the largest storms measured at this site.

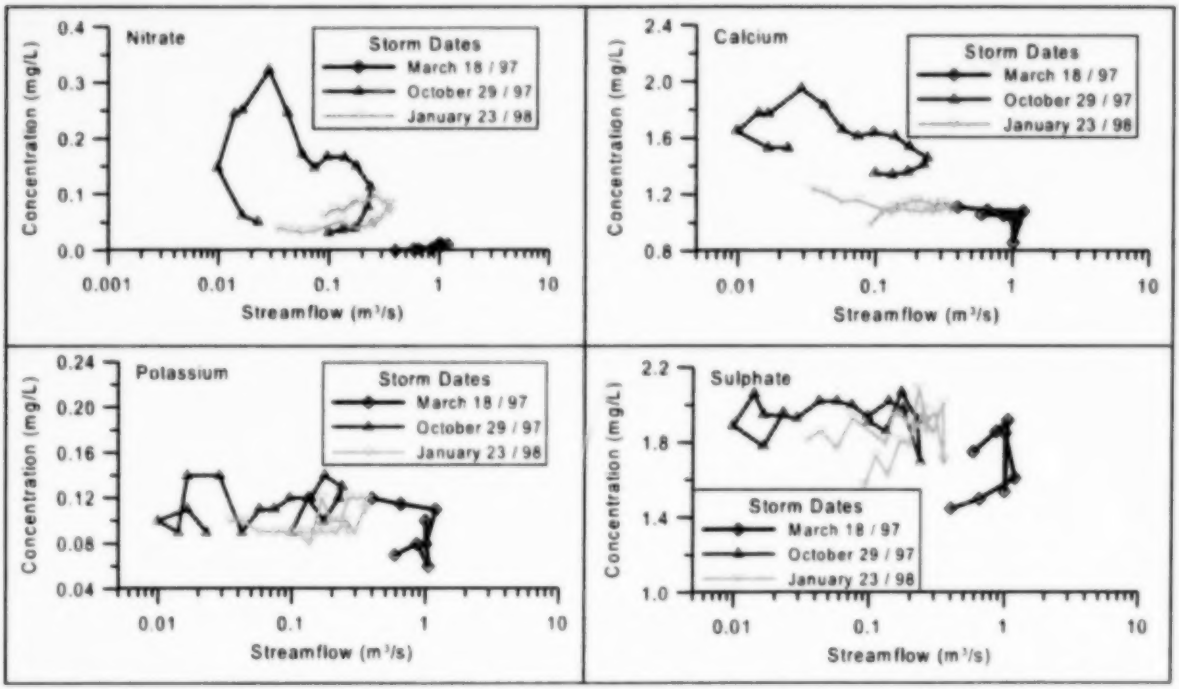

Figure 8. Relationships between concentration and streamflow for nitrate, calcium, potassium and sulphate during the three storms depicted in Figures 5 -7.

storm (Figure 5), all concentrations peak as the streamflow starts to rise. As it rises, concentrations of calcium and nitrate decline due to the dilution effect, while sulphate and potassium concentrations rise again with increasing streamflow after the initial pulse. Throughout the three events, calcium and nitrate levels generally decline, while sulphate and potassium remain relatively constant on average. Nitrate continues to exhibit pulse behaviour during each storm, but the overall concentration declines throughout the season. Calcium and sulphate respond to storms in an opposite manner: calcium concentrations decrease, while sulphate levels increase, with increasing streamflow during storms.

Relationships between concentration and streamflow for each chemical during each event are poorly defined, with the possible exception of calcium for the January event, and nitrate for the March event (Figure 8). Hysteresis is evident in the relationships for both nitrate and calcium, but not for potassium or sulphate. Both chemicals decline in concentration throughout the season, but the three relationships for calcium suggest a general relationship between calcium concentration and streamflow, while for nitrate, the during-storm trend is opposite to the seasonal trend. Potassium concentrations appear unrelated to streamflow, both as a general trend, and for individual storms, while a slight decline in sulphate levels throughout the three storms is evident; this suggests an overall (poorly defined) relationship between sulphate concentration and streamflow derived from lumping the storms together.

4.2 RELATIONSHIPS BETWEEN CONCENTRATION AND STREAMFLOW.

The above observations suggested a set of variables that could potentially be used in equations to predict chemical concentrations (Table 2). The variables "time since the start of the season" (SD) and "time since the last storm" (T_{PP}) are related to specific storms (Table 3). Interactions between the predictors were also considered in the analysis. The procedure described under "Data Analysis" was used to derive general equations to predict chemical concentrations as a function of streamflow, accounting for the seasonal and hysteresis effects (Table 4).

There are two alternate sets of equations, depending on how the seasonal trend is treated (Table 4). One approach is to use a classification variable, S_i, that divides up the water year into fall and winter/spring periods (Table 4a). In the alternative approach, the seasonal trend noted above is treated as a continuous variable by introducing the variable SD (Table 2) into the analysis (Table 4b). It also allows the time between storms (T_{PP}) to be incorporated into the model. The former approach lends itself better to a graphical depiction of the relationships between concentration and streamflow (Figures 9-11), but is somewhat arbitrary, and some data points may get incorrectly classified as a result. For example, there is considerable overlap between fall and winter periods at F5 (Figures 9-11, middle graphs). The latter approach results in a better R^2 for most chemicals.

Either way, there is a complex interaction between the log of streamflow, seasonal effect and hysteresis and that influences concentrations of base cations (Figures 9 and 10), bicarbonate (Figure 11) as well as sulphate, aluminum and silica. Concentrations were generally higher in the fall than the winter/spring, and where there was a significant hysteresis effect, were higher for rising than falling streamflow.

The behaviour of chemical concentrations with respect to streamflow at F4 and F5 were similar, but F6 exhibited different behaviour from the other two creeks, in that there was more variability in the relationship between concentration and streamflow throughout the season. Concentrations at all three creeks were related to the log of streamflow ($\ln(Q_s)$). In some cases, there was an interaction between season and streamflow to produce different slopes in the relationship between fall and winter. This was true of calcium on F4 (Figure 9, lower graph) and bicarbonate on F5 (Figure 11, middle graph). However, at F6, concentrations were not related to streamflow during the winter. It was necessary to define another season variable S_2 to deal with a change in slope of the relationships between concentration and streamflow that occurred about 45 days after the start of the season (Table 4a, Figure 12).

There was no relationship between concentration and streamflow during the winter. However, this is an artifact of lumping the data for winter and spring storms together. For example, in the winter of 1997, most storms exhibited the normal negative relationship between base cations and streamflow, but during the storm that occurred on March 17-18, the opposite trend was

Table 2. Factors that could potentially affect concentrations, and variables used to represent them.

Factor affecting Chemical Concentration	Independent variables used to represent factors.		
Season	S1 = 0 for winter/spring S1 = 1 for fall	S2 = 0 for late fall to spring S2 = 1 for early fall	S3 = 0 for winter S3 = 1 for fall/spring
Hysteresis	R/F = 0 for rising streamflow R/F = 1 for falling streamflow		
Time since start of season	SD = number of days since the first fall storm to cause streams to start flowing		
Time since last storm	T_{PP} = number of days between storm peaks.		
Specific streamflow (L/s/ha)	$\ln(Q_s)$		
Base flow	BF for base flow as a continuous variable W = 0 for classification of low base flow (dry antecedent conditions) W = 1 for classification of high base flow (wet antecedent conditions)		

Table 3. Summary of storms with complete water chemistry sampling

Start Date	Peak Flow	Antecedent Base Flow	Time since Last Storm	Time since start of season	Peak concentration of nitrate pulse
F4:	Q_p (m^3/s)	BF (m^3/s)	T_{ss} (days)	SD (days)	NO_3-p (mg/L)
10/14/96 4:45	0.047	0.001	164.200	3.573	0.161
10/17/96 12:45	0.043	0.006	3.458	7.031	0.000
10/21/96 16:00	0.021	0.006	4.385	11.417	0.000
10/23/96 7:45	0.000	0.013	1.531	12.948	0.000
10/27/96 21:00	0.234	0.010	4.469	17.417	0.000
11/7/96 20:00	0.030	0.008	11.510	28.927	0.025
11/12/96 6:00	0.042	0.007	4.333	33.260	0.021
11/26/96 2:15	0.198	0.004	30.500	47.298	0.087
11/27/96 16:00	0.181	0.111	0.708	47.917	0.000
12/7/96 8:15	0.023	0.012	7.760	58.760	0.016
12/10/96 1:45	0.028	0.012	1.979	60.740	0.013
1/28/97 22:00	0.142	0.005	10.365	111.219	0.033
3/17/97 12:15	0.517	0.007	10.854	158.365	0.018
4/15/97 3:00	0.178	0.009	15.698	187.378	0.024
5/4/97 23:45	0.056	0.014	6.552	206.979	0.012
5/30/97 17:15	0.031	0.007	25.688	232.667	0.113
6/17/97 2:00	0.014	0.002	17.375	250.042	0.044
11/22/97 20:30	0.030	0.0034	25.688	71.042	0.068
12/14/97 9:30	0.080	0.003	22.800	93.844	0.153
12/27/97 17:00	0.076	0.016	12.729	106.573	0.113
1/13/98 13:00	0.101	0.001	18.469	123.042	0.278
1/23/98 5:00	0.130	0.041	2.188	134.000	0.074
3/9/98 2:45	0.049	0.010	19.750	180.052	0.099
3/21/98 23:30	0.035	0.007	9.880	189.938	0.086
F5:					
12/10/95 5:30	0.247	0.018	12.02	32.86	0.033
12/12/95 17:45	0.328	0.099	1.64	35.28	0.016
12/15/95 4:00	0.131	0.153	0.90	37.80	missed peak
1/8/96 6:00	0.092	0.022	6.18	61.80	0.034
1/13/96 10:30	0.233	0.034	5.75	67.07	0.371
2/7/96 13:15	0.095	0.004	24.64	92.19	0.209
10/23/96 7:00	0.076	0.025	6.55	19.19	0.585
10/27/96 22:00	0.229	0.035	3.54	23.81	0.211
11/26/96 8:30	0.213	0.014	30.46	53.26	0.132
3/14/97 0:00	1.199	0.016	5.62	160.90	0.043
4/13/97 19:00	0.113	0.026	2.13	197.69	0.070
4/22/97 20:00	0.096	0.040	3.09	206.73	0.019
5/5/97 3:00	0.068	0.022	5.65	213.02	0.010
10/29/97 18:30	0.248	0.012	20.91	45.60	0.323
11/6/97 8:15	0.137	0.012	7.59	53.18	0.056
12/15/97 20:30	0.086	0.019	16.59	92.69	0.123
12/27/97 20:00	0.168	0.017	12.47	104.67	0.105
1/14/98 8:00	0.113	0.017	18.75	122.17	0.250
1/19/98 0:00	0.148	0.082	1.83	126.83	0.092
1/23/98 5:00	0.354	0.066	4.46	131.04	0.099
3/9/98 2:30	0.047	0.018	19.29	175.94	0.077
3/22/98 2:00	0.016	0.032	16.73	188.92	0.052
F6:					
10/17/96 12:15	0.032	0.013	220.010	9.271	6.737
10/23/96 9:30	0.037	0.015	7.240	7.510	0.010
10/27/96 22:00	0.085	0.022	10.680	10.958	0.037
11/26/96 0:15	0.091	0.006	14.520	41.510	0.164
12/30/96 9:15	0.077	0.005	35.169	76.698	missed peak
1/18/97 6:30	0.052	0.015	8.271	94.698	0.012
1/29/97 13:45	0.027	0.010	10.031	104.729	0.070
2/13/97 22:30	0.029	0.007	20.138	124.865	missed peak
3/17/97 10:00	0.152	0.008	27.583	152.448	0.259
4/19/97 18:45	0.033	0.015	9.200	184.677	0.025
4/22/97 19:45	0.028	0.021	2.813	187.490	0.019
5/5/97 12:15	0.024	0.016	9.333	201.906	0.019
10/3/97 23:45	0.050	0.030	15.410	1.031	0.124
10/8/97 4:45	0.060	0.022	5.125	6.156	0.105
10/28/97 22:00	0.060	0.008	20.688	26.844	0.194
11/23/97 12:00	0.043	0.006	30.896	57.740	missed peak
12/15/97 11:15	0.026	0.008	17.708	75.448	0.101
12/28/97 0:30	0.026	0.008	10.833	86.281	0.069
1/14/98 7:15	0.040	0.007	4.260	103.177	0.051
1/18/98 21:30	0.056	0.016	16.896	107.438	0.148
1/23/98 7:00	0.077	0.024	9.583	112.760	0.108
2/12/98 4:30	0.036	0.014	20.240	133.000	0.145
2/18/98 20:00	0.033	0.015	8.438	141.438	0.123
3/9/98 0:00	0.017	0.010	21.406	162.844	0.068

observed (Figure 12). After this, the normal negative trend was restored, but during the period from mid-May to the end of June, the slope of the relationship was much steeper than for other periods. Thus, there were well-defined relationships between base cation concentration and streamflow for isolated periods, but it was very difficult to define a general relationship of concentration as a function of streamflow and season.

Using the alternate approach described above, whereby the seasonal effect is represented by continuous variables, the resultant equations have higher R^2 scores in most cases, but are more complex (Table 4b). The classification variables used to represent seasons are still significant, but in most cases, the time since the beginning of the season (SD) is also significant. Time since the previous storm (T_{ss}) is also significant, most notably at F6 for all chemicals except calcium and aluminum, and also for bicarbonate at F4, and for silica and aluminum at F5. The interactions between seasonal classification variables and $\ln(Q_p)$, between SD and $\ln(Q_p)$ and between T_{ss} and $\ln(Q_p)$ are also significant, but in most cases, different interaction variables are used. This is particularly true of F6 (Table 4b).

4.3 NITRATE BEHAVIOUR

Nitrate behaviour proved to be the most difficult to characterize of all the chemicals that were measured. If the average nitrate concentration is calculated for each storm, that averaged concentration was found to decline throughout the fall /winter season, and then to rise again in the spring. However, the storm-averaged concentration is not a particularly useful quantity. Pulses of nitrate generally occur in response to storms, around the initial rise in streamflow. However, the timing, duration and magnitude of the pulses varies considerably from storm to storm and from creek to creek. For a given storm, the magnitude of the pulse (i.e., the peak concentration) is generally comparable at F5 and F6, and lower at F4, and is not related to peak streamflow (Figure 13). The hydrograph of the event of November 25, 1996, was double-peaked at all three creeks. At F5, there were two nitrate pulses, occurring on the rising limb of each hydrograph peak, whereas nitrate concentration at F4 did not respond to the second peak, and at F6 the response was not different from background concentration variability.

Although it was not possible to develop a general relationship between concentration and either streamflow or time during the season the peak concentration of the nitrate pulses ([NO_3-p]) was related to the amount of time elapsed since the last storm (T_{ss}, Table 3). In each case, the relationship was defined by a power function. However, there were also other factors that influenced those relationships, which were different for each creek (Figure 14). At F4, there were parallel relationships between [NO_3-p] and T_{ss} where the intercept of the relationship was lower in the fall than at other times of the year. This led to the definition of a third seasonal classification variable Ss, such that Ss is 1 for the fall and spring and 0 for winter. Peak concentrations of nitrate pulses are lower in the fall than in the winter or spring. For F4, the equation defining peak nitrate pulse concentration is:

5. $[NO_3 - p] = e^{(0.756 \ln T_{ss-p}) - 1.198 Ss - 4.21}$ ($R^2 = 70.2\%$)

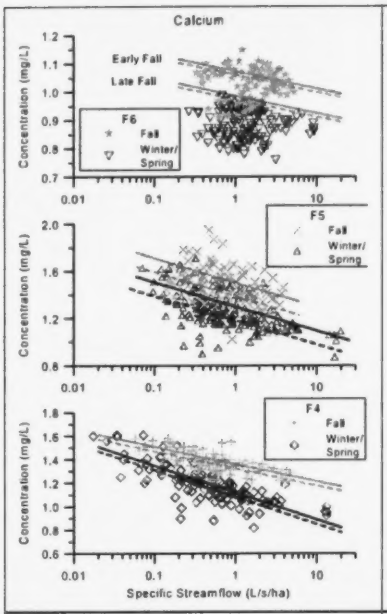

Figure 9. Calcium concentration as a function of season and streamflow. The brown and black lines represent regressions for fall and winter/spring, and the solid and dashed lines represent relationships for rising and falling streamflow, respectively.

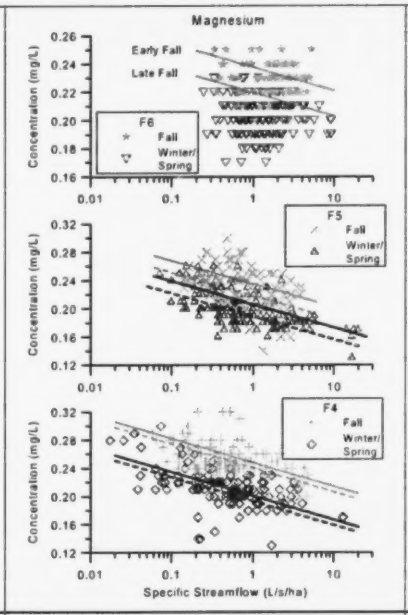

Figure 10. Magnesium concentration as a function of season and streamflow. The brown and black lines represent regressions for fall and winter/spring, and the solid and dashed lines represent relationships for rising and falling streamflow, respectively.

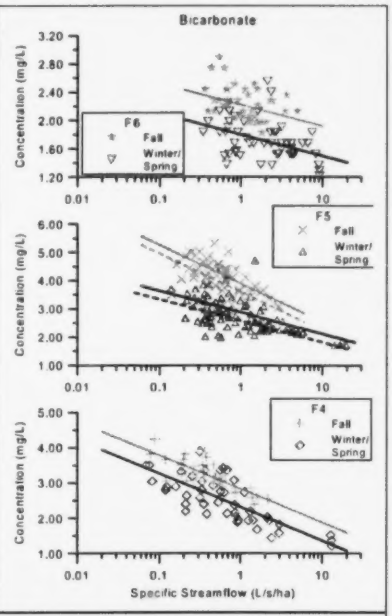

Figure 11. Bicarbonate concentration as a function of season and streamflow. The brown and black lines represent regressions for fall and winter/spring, and the solid and dashed lines represent relationships for rising and falling streamflow, respectively.

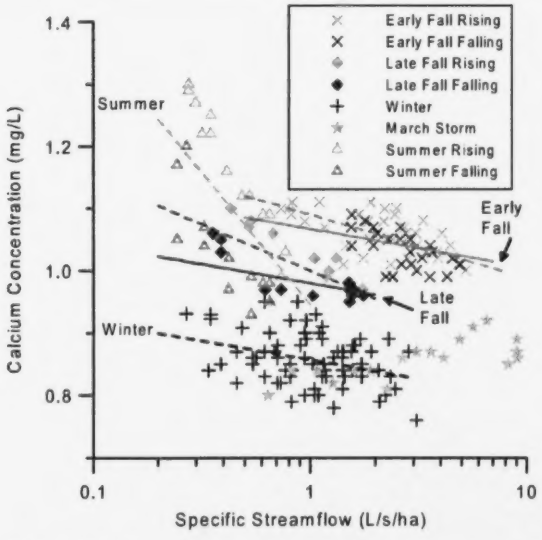

Figure 12. Calcium vs. Q, at F6, for selected storm periods in the 1996-97 season. The solid lines represent equation 2, while the dashed lines represent relationships specific to each period, ignoring hysteresis.

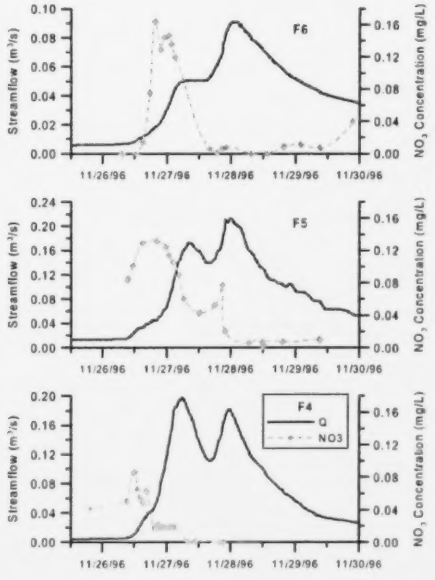

Figure 13. Streamflow and nitrate concentrations for November 26, 1996 storm at F4, F5 and F6.

Table 4a. Results of regression analysis of chemical concentrations vs. streamflow using classification variables to represent seasonal effect. F4 and F5: coefficients of equations of the following form:

1. $[C] = b_0 - b_1 \ln(Q_s) + b_2 S_1 + b_3 RF + b_4 S_1 \cdot \ln(Q_s) + b_5 RF \cdot \ln(Q_s)$

Chemical	Equation Coefficients							
F4:	b_0	b_1	b_2	b_3	b_4	b_5	R^2(%)	s.e.
Calcium	1.115	-0.1004	0.2420	-0.0377	0.0362	0	72.3	0.0924
Magnesium	0.201	-0.0148	0.0473	-0.0077	0	0	66.1	0.0215
Sodium	0.770	-0.0571	0.2560	-0.0425	0	0	61.1	0.1221
Potassium	0.067	-0.0106	0	0	0	0.0076	11.1	0.0305
Aluminum	0.102	0.0166	-0.0196	0	0	0	60.6	0.0192
Silica	0.984	-0.2660	0.3470	0	-0.2950	0.1610	39.0	0.7410
Bicarbonate	2.321	-0.4140	0.5148	0	0	0	73.5	0.3484
Sulphate	1.386	-0.0619	0.2751	0	0	0	34.8	0.2250
F5:								
Calcium	1.297	-0.0894	0.2035	-0.1157	0	0	57.3	0.124
Magnesium	0.206	-0.0143	0.0292	-0.0169	0	0	54.7	0.0197
Sodium	0.966	-0.0486	0.1580	-0.0556	0	0	42.0	0.1105
Potassium	0.086	0.0031	0.0167	0	0	0	13.8	0.0213
Aluminum	0.034	0	-0.0055	0	0	0	3.0	0.0138
Silica	1.941	-0.4589	0	-0.2489	0	0	31.0	0.7089
Bicarbonate	2.864	-0.4830	1.1135	-0.2664	0	0.1694	74.0	0.4576
Sulphate	1.900	-0.0216	0.0791	0	0	0	6.2	0.1713

Note: In these equations, [C] denotes the concentration (mg/L) of a given chemical.

Table 4a. (continued) F6: coefficients of equations of the following form:

2. $[C] = b_0 + b_1 \ln(Q_s) + b_2 S_1 + b_3 S_2 + b_4 S_1 \cdot \ln(Q_s) + b_5 S_2 \cdot \ln(Q_s) + b_6 RF$

Chemical	Equation Coefficients								
F6:	b_0	b_1	b_2	b_3	b_4	b_5	b_6	R^2(%)	s.e.
Calcium	0.894	0	0.0916	0.0875	-0.0269	0	-0.0122	72.6	0.0153
Magnesium	0.202	0	0.0177	0.0180	-0.0073	0	0	59.5	0.0118
Sodium	0.951	0	0.179	0.105	-0.0314	0	0	60.4	0.1041
Potassium	0.0736	0	0	0.0137	0	0	0	4.9	0.0282
Aluminum	0	0	0	0	0	0	0	N.S.R.	N.S.R.
Silica	0.936	0	0	0	-0.178	0	0.0846	11.9	0.2569
Bicarbonate	1.80	-0.131	0.423	0	0	0	0	57.3	0.2340
Sulphate	2.01	0	0	0	0	0.0381	0.0613	12.3	0.1332

Table 4b. Results of regression analysis of chemical concentrations vs. streamflow incorporating continuous variables to represent seasonal effect. For F4 and F5: coefficients of equations of the following form:

3. $[C] = b_0 + b_1 \ln(Q_s) + b_2 S_1 + b_3 S_1 \ln(Q_s) + b_4 SD + b_5 SD \cdot \ln(Q_s) + b_6 T_{p-p} + b_7 T_{p-p} \cdot \ln(Q_s) + b_8 R/F + b_9 R/F \cdot \ln(Q_s)$

Chemical	Equation Coefficients										R^2(%)	s.e.
F4:	b_0	b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8	b_9		
Calcium	1.11	-0.0481	0.254	0	0	-0.000308	0	0	-0.0402	0	73.9	0.0903
Magnesium	0.22	0	0.035	-0.0095	-0.00012	-0.000097	0	0	-0.0086	0	68.8	0.0201
Sodium, Potassium, Aluminum, Silica	same equation as in Table 4a											
Bicarbonate	2.29	-0.3590	0.566	0	0	0	0.00703	0	0	0	78.3	0.2895
Sulphate	1.72	-0.0577	0	0	-0.00200	0	0	0	0	0	37.8	0.2164
F5:												
Calcium	1.29	0	0.209	-0.0642	0	-0.000604	0	0	-0.1090	0	60.5	0.1198
Magnesium	0.21	0	0.030	-0.0114	0	-0.000090	0	0	-0.0160	0	55.9	0.0195
Sodium	1.08	-0.0555	0.083	0	-0.00085	0	0	0	-0.0549	0	48.9	0.1040
Potassium	same equation as in Table 4a											
Aluminum	0.03	0.0034	-0.009	0	0	0	0.00046	0	0	0	17.9	0.0128
Silica	3.00	-0.2080	-0.544	0	-0.00783	-0.002520	-0.01210	-0.0134	-0.1620	0.238	46.6	0.6308
Bicarbonate	2.86	-0.4830	1.110	0		0	0	0	-0.2660	0.169	74.0	0.4576
Sulphate	2.16	0	-0.085	0	-0.00198	-0.000310	0	0	0	0	26.2	0.1521

Table 4b (continued). F6: coefficients of equations of the following form:

4. $[C] = b_0 + b_1 S_1 + b_2 S_2 + b_3 S_3 \cdot \ln(Q_s) + b_4 SD + b_5 SD \cdot \ln(Q_s) + b_6 T_{p-p} + b_7 T_{p-p} \cdot \ln(Q_s)$

Chemical	Equation Coefficients								R^2(%)	s.e.
F6:	b_0	b_1	b_2	b_3	b_4	b_5	b_6	b_7		
Calcium	0.816	0.116	0.134	-0.0376	0.000696	-0.000274	0	0	62.0	0.0614
Magnesium	0.019	0.0211	0.0244	-0.0115	0.000104	-0.000036	0.000096	0	51.7	0.0146
Sodium	1.10	0.0987	0	-0.0109	-0.00107	-0.000207	0.000913	0	67.4	0.0947
Potassium	0.079	0	0	0	-0.000086	0.000063	0.000165	0	17.1	0.0266
Aluminum	0.028	0	0	0	0.000025	0.000012	0	0	5.3	0.0089
Silica	0.883	0	0.139	0	0	0	0.00910	-0.00192	55.6	0.5748
Bicarbonate	1.22	0.700	0.327	0	0.00393	0	0	-0.0122	64.9	0.2143
Sulphate	2.13		0	0.0157	-0.000671	0	-0.00110	0	18.6	0.1313

At F5, there were also parallel relationships, but the factor that distinguishes the upper curve from the lower one is antecedent base flow, rather than season. If base flow is high, the magnitude of the nitrate pulse is higher for a given time between storms than if base flow is low. The division occurs at a base flow of 0.0225 m3/s. A dummy variable W was defined such that for low base flow (i.e., base flow less than 0.0225 m3/s) W = 0, and otherwise, W = 1. This results in the following equation to define peak nitrate pulse concentration for F5:

6. $[NO_3 - p] = e^{(0.311\ln T_{p-p}) - 5.82)} = 0.00297 T_{p-p})^{1.3131}$

(R^2 = 59.0%)

At F6, peak nitrate pulse concentration was related to the time since the last storm, with no additional factors:

7 $[NO_3 - p] = e^{(0.521\ln T_{p-p}) + 2.32W - 6.42)}$

(R^2 = 68.4%)

4.4 ORIGIN OF CHEMICALS

The behaviour of many chemicals can be partly explained in relation to their likely origin. Information on the origin of chemicals can be derived from inter-relationships among the chemical concentrations. In general, the chemicals found in the water of Flume Creek can be derived from three sources:

- Mineral weathering,
- Input from precipitation, and,
- Biological activity.

The latter source can also interact with the first two sources. In addition, plants use some chemicals but not others, and different chemicals are generated from different components of the terrestrial watershed (Table 5). Concentrations of chemicals associated with the forest floor are often positively correlated with streamflow, while those of chemicals associated with mineral soil are usually negatively correlated with streamflow (Hudson and Golding, 1997a).

Base cations and silica are derived primarily from mineral weathering, but are also present in precipitation (Table 6). Bicarbonate is derived from a combination of weathering and soil respiration. However, if the bicarbonate concentration is used as an index of the degree of weathering, then plots of base cation concentration vs. bicarbonate concentration illustrate the relative contribution of mineral weathering and other sources to the concentrations of those components in streamflow (Figure 13). The regression line for silica passes nearly through the origin, reflecting the fact that silica is derived almost entirely from mineral weathering. The intercept of the relationship is 0.26, which matches the mean concentration of silica in rainfall collected at forested sites (Table 6). Similarly, the intercepts of the regressions for calcium, sodium and magnesium closely match the mean concentrations of those ions in precipitation at forested sites. Thus, the intercepts of the relationships between cation and bicarbonate concentrations represent the contribution from external sources.

If these intercepts are compared with the mean concentrations in streamflow (Table 1), this suggests that on the average, 63%

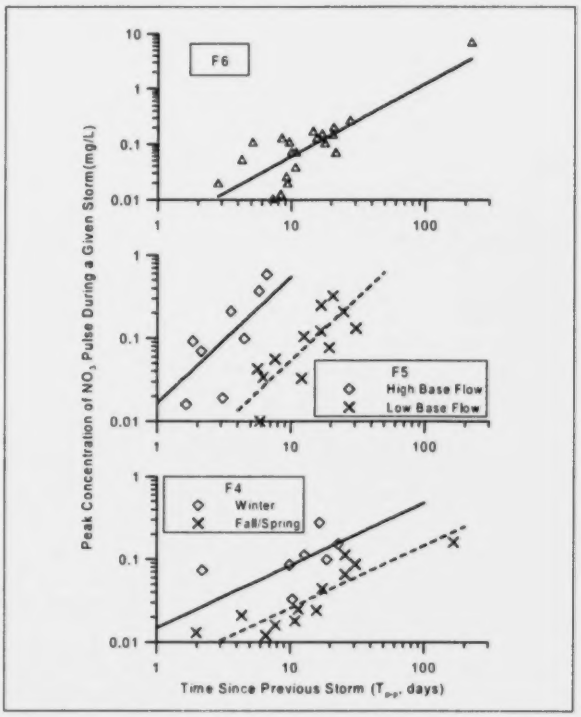

Figure 14. Peak nitrate pulse concentration in relation to time since previous storm for F4, F5 and F6.

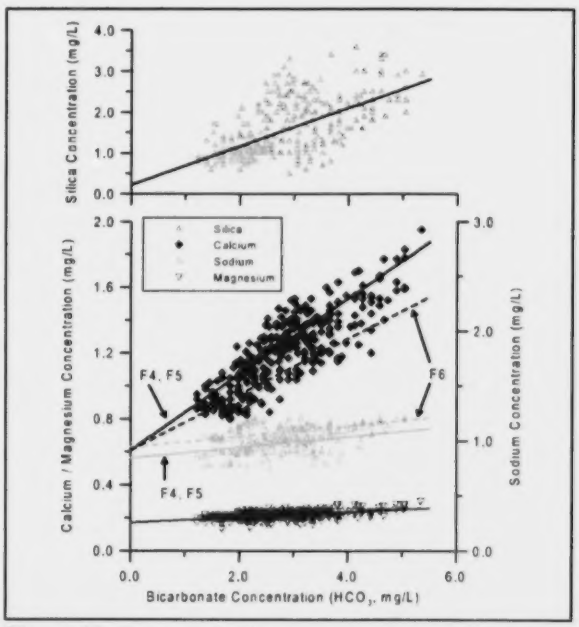

Figure 15. Cation and silica concentrations vs. bicarbonate concentration.

Table 5. Potential factors affecting chemical concentrations in streams.

	Weathering	Rainfall	Bacterial Activity	Plant Uptake	Forest Canopy	Fallout	Associated With:
SiO_4	X				X	X	Mineral Soil
Ca	X	X			X	X	Mineral Soil
Na	X	X			X	X	Mineral Soil
Mg	X	X			X	X	Mineral Soil
K	X	X		X	X	X	Mineral Soil
Al	X		X				Forest Floor
SO_4	X	X	X	X			Forest Floor
HCO_3	X		X				Mineral Soil
NO_3		X	X	X			Forest Floor
Cl		X				X	Precipitation

Table 6. Summary of mean precipitation chemistry, by year and by forest cover. Also includes the intercepts of the [C] vs. [HCO3] relationships for streamflow samples.

Type of Site	Al	Ca	Cl	Cu	K	Mg	Mn	NH_4	NO_3	Na	SO_4	SiO_4
Open 1997-98	0.00	0.30	0.88	0.02	0.11	0.04	0.00	0.04	0.53	0.22	0.64	0.14
Forest 1997-98	0.00	0.57	0.87	0.11	0.21	0.10	0.01	0.05	0.63	0.50	0.84	0.23
Proportion of Chemical derived from canopy	0.11	0.47	0.00	0.80	0.51	0.61	1.00	0.18	0.16	0.56	0.24	0.39
Intercept of relationship [C] vs. [HCO3]		0.61			0.05	0.17				0.88		0.25

Table 7. Mean concentrations in streamflow and intercepts of cation and silica vs. bicarbonate regressions.

Chemical	Mean Concentrations			Mean concentration in rain	Intercept	Mean Rain/ Mean Streamflow	Proportion not accounted for
	F4	F5	F6				
SiO_4	1.50	1.99	1.18	0.21	0.26	0.14	0.03
Ca	1.36	1.33	0.98	0.57	0.61	0.47	0.03
Na	0.98	1.00	1.07	0.50	0.88	0.49	0.37
Mg	0.25	0.23	0.22	0.10	0.16	0.43	0.26
K	0.08	0.09	0.09	0.21	0.05	2.35	-1.79

Table 8. Estimated contribution (%) of sources of chemicals to streamflow.

	Weathering	Rainfall	Forest	Unknown
Ca	50	25	22	3
Na	14	22	27	37
Mg	31	17	26	26
K	44	56	0	N/A
SO_4		22	24	54
HCO_3	50	0	50	0
NO_3	0			100
Cl		82	0	18

of the base cations are derived from sources other than mineral weathering, 47% come from precipitation, and the remainder come from unknown sources (Table 7). A comparison between the mean precipitation chemistry at open and forested sites indicates that about 50% of the calcium, potassium and sodium and 39% of the silica delivered to the watershed through precipitation are derived from the forest canopy. Therefore, this suggests that about 23% of the calcium, magnesium and sodium in streamflow are either recycled by the forest or derived from atmospheric fallout.

The origin and fate of potassium is more complex since it is an essential nutrient used by trees. Note that the average concentration of potassium in rain is greater than that in streamflow. Although potassium is also a weathering product, it is not correlated with bicarbonate (R^2 = 3%). Most of the potassium that is produced by weathering or delivered through precipitation is absorbed by the biomass. Chloride concentrations in rainfall and streamflow are closely matched, indicating that chloride is derived from rainfall, and suggesting that sea salt is the most likely source of precipitation-derived cations. Nitrate is also partly derived from atmospheric sources, and is accumulated in the biomass.

These results allow the relative contribution of different sources of chemicals to the chemical load in streamflow to be estimated (Table 9). The fact that at most only 50% of the base cations in streamflow is derived from weathering helps to explain the difficulty in defining the relationships between concentrations and streamflow. There is an inverse relationship between the mean R^2 of the relationships reported in Table 4 and the unknown component in Table 9. The fact that the mean R^2 of the relationships between calcium and bicarbonate vs. streamflow are similar suggests that about 50% of the bicarbonate is derived from weathering. By inference, the rest is derived from soil respiration, since the pH of rainfall is too low to support bicar-

bonate. The relative sources of nitrate cannot be estimated by these methods, because nitrate is not a weathering product. Nitrate is derived from input by rainfall and nitrification, the process by which bacteria convert ammonium (derived from breakdown of organic matter) to nitrate by oxidization.

5.0 DISCUSSION

The results of this modeling exercise indicate that in most cases there are logarithmic relationships between chemical concentrations and streamflow, but that effect is intertwined with the general effect of season. In most cases, season is the dominant effect, resulting in a high degree of complexity in the equations (Tables 4a and 4b). The seasonal effect operates not only on the average concentration during storms, but also on the slope of the relationship between concentration and streamflow. At F4 and F5, the interaction between seasonal classification and streamflow is most commonly superimposed on a general relationship between concentration and ln(Qs). At F6, the relationship between concentration and streamflow commonly interacts with either the time since the beginning of the season or the time since the last storm. This indicates that the effect of season is stronger at F6 than it is at F4 and F5. The most likely reason for this is that F6 is a lower elevation catchment than the other two watersheds.

Part of the reason for the difficulty in establishing the above relationships lies in the apparent mixed origin of most chemicals. In subalpine watersheds in the interior of BC, weathering was the dominant control on base cations and silica, resulting in simple, well defined logarithmic relationships with streamflow (Hudson & Golding, 1997b). The apparent effect of the forest itself on these parameters at Flume Creek increases the unpredictability of the effects of harvesting on the concentrations of those chemicals.

Nitrate was the most difficult chemical to characterize due to its pulse behaviour. However, nitrate is probably the most important chemical parameter because of its importance as an essential nutrient and to its volatility. It is generally accepted as the most sensitive indicator of ecosystem disturbance (Binkley and Brown, 1993). According to one theory, the changes in water chemistry that are observed after forest harvesting might all be linked to changes in nitrate production (Nodvin et al., 1998). Relationships that were established between peak nitrate concentration and time between storms indicate that nitrate is produced and subsequently exported from the watersheds over a short time period. This suggests that harvesting could potentially have a large effect on nitrate concentrations.

The interaction between season and streamflow in their effect on concentration is a subtlety, but it is important to recognize this in order to maximize the value of the pretreatment chemical data at Flume Creek. The dominant cation at F4 and F5 is bicarbonate, whereas at F6, bicarbonate and sulphate are roughly equal in their dominance. Concentrations of calcium and silica are lowest at F6, but are roughly the same at F4 and F5 (Table 1). These comparisons indicate that F6 is likely more sensitive to chemical disturbance from forest harvesting than F4 and F5, whereas the effect of harvesting on water chemistry at F4 and F5 are likely to be similar for similar harvesting patterns. In other words, the chemical characteristics of F4 and F5 are more similar to each other than to F6. This reinforces the appropriateness of F6 as a control creek and of F4 and F5 as treatment creeks, but also stresses the importance of relationships presented in Table 4 as an essential tool to assess the nature of any changes in water chemistry following forest harvesting.

6.0 CONCLUSION

Pre-treatment water chemistry was analysed for three study creeks at the Roberts Creek Study Forest. The chemicals studied are derived primarily from chemical weathering, biological activity and atmospheric sources. Water chemistry was controlled by time during the season, suggesting a buildup of stored chemicals over the dry summer months, followed by a period during which the chemicals are leached from the watershed faster than the rate at which they can be replenished. Within storms, there is a dilution effect that also influences concentrations. These effects interact, resulting in highly complex relationships between chemical concentrations, streamflow and seasonal factors.

This is the first in a series of reports on water chemistry at Flume Creek, and forms in part the basis for assessing the effects of two partial harvesting systems on water chemistry in small S5 and S6 creeks in south coastal B.C.

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